Claims

1. A method for producing a group IB-IIIA-VIA quaternary or higher alloy semiconductor film, the method comprising the steps of:

   (i) providing a metal film comprising a mixture of group IB and group IIIA metals;

   (ii) heat treating the metal film in the presence of a source of a first group VIA element (said first group VIA element being hereinafter referred to as VIA_1) under conditions to form a first film comprising a mixture of at least one binary alloy selected from the group consisting of a group IB-VIA_1 alloy and a group IIIA-VIA_1 alloy; and at least one group IB-IIIA-VIA_1 ternary alloy,

   (iii) heat treating the first film in the presence of a source of a second group VIA_2 element (said second group VIA element being hereinafter referred to as VIA_2) under conditions to convert the first film of step (ii) into a second film comprising at least one alloy selected from the group consisting of a group IB-VIA_1-VIA_2 alloy and a group IIIA-VIA_1-VIA_2 alloy; and the at least one group IB-IIIA-VIA_1 ternary alloy of step (ii); and

   (iv) heat treating the second film of step ((iii)) to form a group IB-IIIA-VIA quaternary or higher alloy semiconductor film.

2. The method according to claim 1, wherein the mixture of the first film of step (ii) is a stable mixture such that the molar ratio of all the group IB-VIA_1 and/or group IIIA-VIA_1 alloys to all the at least one group IB-IIIA-VIA_1 ternary alloy remains substantially constant.

3. The method according to claim 1, wherein the metal film of step (i) is provided on a substrate optionally coated with a metal layer.

4. The method according to claim 3, wherein the metal layer is a Mo layer.

5. The method according to claim 1, wherein the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga.

6. The method according to claim 5, wherein the metal film of step (i) is a Cu-In-Ga alloy metal film.

7. The method according to claim 5, wherein the metal film is a Cu-In alloy metal film.

8. The method according to claim 1, wherein the group VIA_1 element is Se.

9. The method according to claim 1, wherein a source of the group VIA_1 element is a gaseous mixture of H_2Se and at least one inert gas.

10. The method according to claim 9, wherein the inert gas is Ar.

11. The method according to claim 9, wherein the molar concentration of Se relative to the at least one inert gas is from 0.01 to 15 molar percent.

12. The method according to claim 11, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3 molar percent.

13. The method according to claim 1, wherein step (ii) is carried out at a reaction temperature from 300 to 500°C.

14. The method according to claim 13, wherein step (ii) is carried out at a reaction temperature from 350 to 450°C.

15. The method according to claim 13, wherein the metal film of step (i) is heated rapidly to a reaction temperature of between 300 to 500°C within 5 minutes.

16. The method according to claim 1, wherein during step (ii) the metal film of step (i) is exposed to the source of VIA_1 for a period from 10 to 120 minutes.

17. The method according to claim 16, wherein the metal film of step (i) is exposed to the source of VIA_1 for a period from 30 to 60 minutes.

18. The method according to claim 1, wherein the first film of step (ii) has below 50 atomic % of the $V1A_1$ element.

19. The method according to claim 8, wherein the first film of step (ii) has below 50 atomic % of Se.

20. The method according to claim 1, wherein the first film of step (ii) is treated under conditions to ensure that the mixture of the at least one binary alloy and the at least one group IB-IIIA-VIA_1 ternary alloy remains stable.

21. The method according to claim 20, wherein the source of the $V1A_1$ element is removed so as to maintain the stability of the mixture.

22. The method according to claim 20, wherein the first film of step (ii) is exposed to an inert atmosphere for 5 to 20 minutes.

23. The method according to claim 20, wherein the first film of step (ii) is cooled to temperatures below 200°C.

24. The method according to claim 5, wherein the first film of step (ii) comprises a mixture of at least one binary alloy selected from the

group consisting of InSe, CuSe and Ga_2Se_3 and at least one ternary alloy selected from the group consisting of $CuInSe_2$ and $CuGaSe_2$, where VIA_1 is Se.

25. The method according to claim 1 which is for producing a group IB-IIIA-VIA pentenary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film including a mixture of at least one group IB element, a first group IIIA element (the first group IIIA element hereinafter being referred to as $IIIA_1$) and a second group IIIA element (the second group IIIA element hereinafter being referred to as $IIIA_2$);

- step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA_1 alloy, a group $IIIA_1$-VIA_1 alloy and a group $IIIA_2$-VIA_1 alloy and two ternary alloys, namely a group IB-$IIIA_1$-VIA_1 alloy and a group IB-$IIIA_2$-VIA_1 alloy;

- step (iii) comprises heat treating the first film of step (ii) in the presence of a source of VIA_2 under conditions to convert the first film of step (ii) into a second film comprising at least one alloy selected from the group consisting of a group IB-VIA_1-VIA_2 alloy, a group $IIIA_1$-VIA_1-VIA_2 and a group $IIIA_2$-VIA_1-VIA_2 alloy; and the ternary alloys of step (ii); and

- step (iv) comprises heat treating the second film of step (iii) to form a group IB-$IIIA_1$-$IIIA_2$-VIA_1-VIA_2 pentenary alloy semiconductor film.

26. The method of claim 25, wherein the first film of step (ii) includes a mixture of binary alloys in the form of a group IB-VIA_1 alloy, a group $IIIA_1$-VIA_1 alloy and a group $IIIA_2$-VIA_1 alloy and ternary alloys in the form of a group IB-$IIIA_1$-VIA_1 alloy and a group IB-$IIIA_2$-VIA_1 alloy and wherein the second film of step (iii) includes a

mixture of alloys in the form of a group IB-VIA_1-VIA_2 alloy, a group $IIIA_1$-VIA_1-VIA_2 and a group $IIIA_2$-VIA_1-VIA_2 alloy and the ternary alloys of step (ii).

27. The method according to claim 26, wherein step (iv) comprises a first heat treatment step wherein the second film of step (iii) is heated to form a third film comprising a mixture of quaternary alloys selected from the group consisting of a group IB-$IIIA_1$-VIA_1-VIA_2 alloy and a group IB-$IIIA_2$-VIA_1-VIA_2 alloy; and then subjecting the third film to a second heat treatment step wherein the third film is annealed so as to form a group IB-$IIIA_1$-$IIIA_2$-VIA_1-VIA_2 pentenary alloy semiconductor film.

28. The method according to claim 27, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) in the presence of a source of VIA_2 so as to form the third film.

29. The method according to claim 28, wherein the second film of step (iii) is exposed to the source of VIA_2 for a period of from 5 to 10 minutes.

30. The method according to claim 29, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) at a temperature from 450 to 600°C so as to form the third film.

31. The method according to claim 30, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) at a temperature from 500 to 550°C.

32. The method according to claim 27, wherein the second heat treatment step of step (iv) comprises annealing the third film for 15 to 90 minutes.

33. The method according to claim 32, wherein the second heat treatment step of step (iv) comprises annealing the third film at a temperature from 500°C to 600°C.

34. The method according to claim 33, wherein the second heat treatment step of step (iv) comprises annealing the third film at a temperature from 520°C to 580°C.

35. The method according to either one of claims 26 and 27, wherein IB is Cu, $IIIA_1$ is In, $IIIA_2$ is Ga, VIA_1 is Se and VIA_2 is S.

36. The method according to claim 35, wherein the second heat treatment step of step (iv) comprises annealing the third film under conditions so as to form a pentenary alloy having the general formula II:

$$Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2 \quad \ldots\ldots\ldots \quad (I)$$

37. The method according to claim 35, wherein a source of S is a gaseous mixture of H_2S and at least one inert gas.

38. The method according to claim 37, wherein the molar concentration of S relative to the at least one inert gas is from 0.1 to 10 molar percent.

39. The method according to claim 38, wherein the molar concentration of S relative to the at least one inert gas is from 0.3 to 0.5 molar percent.

40. The method according to claim 25, wherein, in step (iii), the first film of step (ii) is heat-treated at a temperature of from 100 to 500°C.

41. The method according to claim 40, wherein, in step (iii), the first film of step (ii) is heat-treated at a temperature of 450°C.

42. The method according to claim 40, wherein, in step (iii), the first film of step (ii) is heat-treated for a period of from 5 to 10 minutes.

43. The method according to claim 25 which is for producing a group IB-IIIA-VIA alloy semiconductor film, and wherein

- step (i) comprises providing a metal film comprising a mixture of Cu, In and Ga;

- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3%, at a temperature of from 350°C to 450°C, for a period of between 30 to 60 minutes, so as to form a first film comprising a mixture of binary alloys in the form of CuSe, InSe, Ga_2Se_3 and the ternary alloys, namely $CuInSe_2$ and $CuGaSe_2$;

- step (iii) comprises heat treating the first film of step (ii) in the presence of a gaseous mixture of H_2S and at least one inert gas, at a temperature from 400°C to 500°C, for a period from 5 to 10 minutes, so as to form a second film comprising a mixture of sulfoselenides in the form of Cu(Se,S), In(Se,S) and Ga(Se,S) and the ternary alloys of step (ii); and

- step (iv) comprises heat treating the second film of step (ii) in the presence of H_2S in Ar, at a temperature of from 500°C to 550°C, for 5 to 10 minutes such that the sulfoselenides react with the ternary alloys of step (ii) to form a third film comprising a mixture of $CuIn(Se,S)_2$ and $CuGa(Se,S)_2$, and subsequently annealing the mixture of $CuIn(Se,S)_2$ and $CuGa(Se,S)_2$ at a temperature of from 520°C to 580°C so as to form a pentenary alloy having the general formula (I).

44. A method for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, the method comprising the steps of:

(i) providing a metal film comprising a mixture of group IB and group IIIA metals;

(ii) heat treating the metal film in the presence of a source of a first group VIA element (said first group VIA element being hereinafter referred to as VIA_1) under conditions to form a first film comprising a mixture of at least one binary alloy selected from the group consisting of a group IB-VIA_1 alloy and a group IIIA-VIA_1 alloy; and at least one group IB-IIIA-VIA_1 ternary alloy, wherein the mixture is a stable mixture such that the molar ratio of all the group IB-VIA_1 and/or group IIIA-VIA_1 alloys to the at least one group IB-IIIA-VIA_1 ternary alloy remains substantially constant, and

(iv) heat treating the first film of step (ii) to form a group IB-IIIA-VIA quaternary alloy semiconductor film.

45. The method according to claim 44, wherein the first film of step (ii) is treated under conditions to ensure that the mixture of the at least one binary alloy and the at least one group IB-IIIA-VIA_1 ternary alloy remains stable.

46. The method according to claim 45, wherein the source of the VIA_1 element is removed so as to maintain the stability of the mixture.

47. The method according to claim 45, wherein the first film of step (ii) is exposed to an inert atmosphere for 5 to 20 minutes.

48. The method according to claim 45, wherein the first film of step (ii) is cooled to temperatures below 200°C.

49. The method according to claim 44, wherein the metal film of step (i) is provided on a substrate optionally coated with a metal layer.

50. The method according to claim 49, wherein the metal layer is a Mo layer.

51. The method according to claim 44, wherein the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga.

52. The method according to claim 51, wherein the metal film of step (i) is a Cu-In-Ga alloy metal film.

53. The method according to claim 51, wherein the metal film is a Cu-In alloy metal film.

54. The method according to claim 44, wherein the group VIA, element is Se.

55. The method according to claim 44, wherein a source of the group VIA_1 element is a gaseous mixture of H_2Se and at least one inert gas.

56. The method according to claim 55, wherein the inert gas is Ar.

57. The method according to claim 55, wherein the molar concentration of Se relative to the at least one inert gas is from 0.01 to 15 molar percent.

58. The method according to claim 57, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3 molar percent.

59. The method according to claim 44, wherein step (ii) is carried out at a reaction temperature from 300 to 500°C.

60. The method according to claim 59, wherein step (ii) is carried out at a reaction temperature from 350 to 450°C.

61. The method according to claim 59, wherein the metal film of step (i) is heated rapidly to a reaction temperature of between 300 to 500°C within 5 minutes.

62. The method according to claim 44, wherein during step (ii) the metal film of step (i) is exposed to the source of VIA_1 for a period from 10 to 120 minutes.

63. The method according to claim 62, wherein the metal film of step (i) is exposed to the source of VIA_1 for a period from 30 to 60 minutes.

64. The method according to claim 44, wherein the first film of step (ii) has below 50 atomic % of the $V1A_1$ element.

65. The method according to claim 54, wherein the first film of step (ii) has below 50 atomic % of Se.

66. The method according to claim 44, wherein the first film of step (ii) comprises a mixture of at least one binary alloy selected from the group consisting of InSe, CuSe and Ga_2Se_3 and at least one ternary alloy selected from the group consisting of $CuInSe_2$ and $CuGaSe_2$, where VIA_1 is Se.

67. The method according to claim 44 which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film including a mixture of at least one group IB element, a first group IIIA element (the first group IIIA element hereinafter being referred to as $IIIA_1$) and a second group IIIA element (the second group IIIA element hereinafter being referred to as $IIIA_2$);

- step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA_1 alloy, a group $IIIA_1$-VIA_1 alloy and a group $IIIA_2$-VIA_1 alloy and a ternary alloy being a group IB-$IIIA_1$-VIA_1 alloy;

- step (iv) comprises heat treating the first film of step (ii) to form a group IB-$IIIA_1$-$IIIA_2$-VIA_1 quaternary alloy semiconductor film.

68. The method according to claim 67, wherein the heat treatment of step (ii) is carried out at a reaction temperature of 400°C.

69. The method according to claim 67, wherein step (iv) comprises a first heat treatment step wherein the first film of step (ii) is heated and then subsequently a second heat treatment step wherein the first film is annealed so as to form a group IB-$IIIA_1$-$IIIA_2$-VIA_1 quaternary alloy semiconductor film.

70. The method according to claim 69, wherein the first heat treatment step of step (iv) comprises heating the first film of step (ii) to a reaction temperature of from 100 to 600°C.

71. The method according to claim 69, wherein the second heat treatment step of step (iv) comprises first annealing the first film of step (ii) in the presence of an inert gas and then subsequently annealing the first film in the presence of a source of VIA_1.

72. The method according to claim 71, wherein the first film of step (ii) is first annealed in the presence of the inert gas at a temperature of from 100 to 600°C.

73. The method according to claim 72, wherein the first film of step (ii) is first annealed in the presence of the inert gas at a temperature of from 500 to 550°C.

74. The method according to claim 72, wherein the first film is fist annealed in the presence of the inert gas for a period of from 10 to 60 minutes.

75. The method according to claim 71, wherein the first film of step (ii) is subsequently annealed in the presence of a source of VIA_1 for at least 30 minutes.

76. The method according to claim 75, wherein the first film of step (ii) is annealed in the presence of a source of VIA_1 at a temperature of 500°C.

77. The method according to either one of claims 67 and 69, wherein IB is Cu, $IIIA_1$ is In, $IIIA_2$ is Ga, VIA_1 is Se.

78. The method according to claim 77, wherein the quaternary alloy has a formula (II)

$$Cu(InGa)Se_2 \ldots\ldots (II)$$

79. The method according to claim 77, wherein a source of Se is a gaseous mixture of H_2Se and at least one inert gas.

80. The method according to claim 79, wherein the molar concentration of Se relative to the at least one inert gas is 0.12%.

81. The method according to claim 67 which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film comprising a mixture of Cu, In and Ga in elemental or alloy form;

- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at

least one inert gas is from 0.05 to 0.3%, at a temperature of 400°C, for a period of between 30 to 60 minutes, so as to form a mixture of binary alloys in the form of CuSe, InSe, Ga_2Se_3 and a ternary alloy in the form of a $CuInSe_2$ alloy.

- step (iv) comprises subjecting the first film of step (ii) to the following consecutive steps:

  - a first heat treatment step comprising heat treating the first film of step (ii) to a reaction temperature from 500°C to 550°C in 15 to 30 minutes;

  - a second heat treatment step comprising first annealing the first film of step (ii) in Ar(g) at a reaction temperature from 500°C to 550°C for at least 15 minutes; and then secondly annealing the first film of step (ii) in the presence of a gaseous mixture of H_2Se and Ar(g), wherein the molar concentration of Se relative to Ar is 0.12% so as to form a quaternary alloy having the general formula (II).

82 The method according to claim 44, which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film including a mixture of at least one group IB element and a group IIIA element;

- step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA_1 alloy, a group IIIA-VIA_1, and a ternary alloy being a group IB-IIIA-VIA_1 alloy; and

- step (iv) comprises heat treating the first film of step (ii) in the presence of a source of VIA_2 so as to form a group IB-IIIA-VIA_1-VIA_2 quaternary alloy semiconductor film.

83 The method according to claim 82, wherein step (iv) comprises a first heat treatment step wherein the first film of step (ii) is heated and then subsequently a second heat treatment step wherein the first film of step (ii) is annealed so as to form a group IB-IIIA-VIA_1-VIA_2 quaternary alloy.

84. The method according to claim 83, wherein the first heat treatment step of step (iv) comprises heating the first film of step (ii) to a reaction temperature from 100 to 600°C.

85. The method according to claim 83, wherein the second heat treatment step of step (iv) comprises annealing the first film of step (ii) in the presence of a source of VIA_2.

86. The method according to claim 85, wherein the first film of step (ii) is annealed in the presence of the source of VIA_2 at a temperature from 100 to 600°C.

87. The method according to claim 86, wherein the first film of step (ii) is annealed in the presence of the source of VIA_2 at a temperature from 500 to 550°C.

88. The method according to claim 87, wherein the first film of step (ii) is annealed in the presence of a source of VIA_2, at a temperature of 500°C.

89. The method according to claim 85, wherein the first film of step (ii) is annealed in the presence of a source of VIA_2 for at least 30 minutes.

90. The method according to either one of claims 82 and 83, wherein IB is Cu, the group IIIA element is In, VIA_1 is Se, VIA_2 is S.

91. The method according to claim 90, wherein the quaternary alloy has a formula (III);

$CuIn(Se_{1-y}S_y)_2$.....(III)

92. The method according to claim 90, wherein a source of S is a gaseous mixture of H_2S and at least one inert gas.

93. The method according to claim 92, wherein the molar concentration of S relative to the at least one inert gas is 0.35 molar percent.

94. The method according to claim 82, which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film comprising a mixture of Cu and In in elemental or alloy form;

- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3% for a period of between 30 to 60 minutes, so as to form a mixture of binary alloys in the form of CuSe and InSe and a ternary alloy, namely $CuInSe_2$; and

- step (iv) comprises subjecting the first film of step (ii) to the following consecutive steps:

  - a first heat treatment step comprising heat treating the first film of step (ii) to a reaction temperature from 500°C to 550°C in 15 to 30 minutes;

    - a second heat treatment step comprising annealing the first film of step (ii) in the presence of a gaseous mixture of H2S and Ar(g), at a temperature of from 500oC to 550oC, wherein the molar concentration of S relative to Ar is 0.35%

so as to form a quaternary alloy having the general formula (III).